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## (54) Suspension polymerization of p-methylstyrene.

(57) A process for aqueous suspension polymerization of p-methylstyrene, in which a difficultly soluble phosphate is used as a suspension stabilizer together with sulfonated poly(p-methylstyrene) as an extender.

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ACTORUM AG

# SUSPENSION POLYMERIZATION OF p-METHYLSTYRENE

This invention is directed to the suspension polymerization of p-methylstyrene.

Bead-shaped vinyl polymers are generally produced by suspension polymerization processes in which the monomer is suspended or dispersed in an aqueous medium in the presence of a suspension stabilizer and a polymerization initiator. The suspension stabilizer acts to prevent undesirable agglomeration of the polymerizing monomer and to produce the high molecular weight polymer in bead form. Unstable dispersions result in agglomeration of the polymeric material into large masses.

Suspension stabilizers that are widely used are the difficultly soluble phosphates, such as calcium, strontium, and magnesium phosphates. While under certain conditions these difficultly soluble phosphates serve to stabilize suspensions, they are erratic in behavior. Various materials have been proposed as auxiliary stabilizers or "extenders" for the difficultly soluble phosphate to increase its effectiveness as a suspension stabilizer: The anionic surface active agents, for example, must be used in carefully controlled amounts to avoid adverse effects. In addition, the range of concentrations which may be used is very narrow, making it difficult to follow the commercial practice of varying the polymer bead size by varying the amount of anionic surface active agent. Another proposed type of extender is a soluble salt of alkyl phosphoric acid.

We have now found an extender for use in the polymerization of para-methylstyrene. The extender is used in combination with a difficultly soluble phosphate and, appears to be specific for polymerization of p-methylstyrene. Attempts to use it in suspension polymerization of styrene result in collapse of the suspension.

The present invention provides a process for the aqueous suspension polymerization of p-methylstyrene, in which a difficultly soluble phosphate is used as a suspension stabilizer and, as an extender, sulfonated poly(p-methylstyrene).

The monomer used in the process of this invention is p-methylstyrene. It is possible to use mixtures of methylstyrene isomers which are rich in the p-methylstyrene isomer. Such mixtures preferably contain at least 95 weight percent, preferably 97 to 99 weight percent, p-methylstyrene and less than 0.1, preferably less than 0.05, weight percent o-methylstyrene, with the balance being m-methylstyrene. A typical mixture contains, by weight, about 95 percent p-methylstyrene, about 5 percent m-methylstyrene, and about 0.5 percent o-methylstyrene. The mixtures may be obtained by catalytic dehydrogenation of the mixtures of ethylmethyl benzene isomers described in U. S. Patent No. 4,086,287. The mixtures themselves are described in our DE-OS 2821589.

Using the improved suspension system of this invention, it is possible to use weight ratios of monomer to water of from 60:40 to 30:70. The best efficiencies appear to occur at a 50:50 weight ratio which is the optimum.

"Difficultly soluble" phosphates are those phosphates which are not classifiable as water-soluble phosphates. The term "difficultly soluble" includes in its scope the terms "soluble," "very slightly soluble" and "slightly soluble," given in Hackh's Chemical Dictionary, third edition, page 787; and is intended to mean that more than 100 parts by weight of water are required to dissolve one part by weight of phosphate. The base or metal component of these phosphates may be any metal whose carbonate is also difficultly soluble in water. Thus, the metal may be calcium, barium, strontium, magnesium,

aluminum, zinc, cadmium or iron, all of which give difficultly soluble phosphates.

Phosphates of the type described above as suitable for the practice of the invention may be prepared by precipitation methods. For example, metathetic or double decomposition reactions may be used to obtain precipitates of difficultly soluble phosphates, such as the reaction of ortho-phosphoric acid with an appropriate oxide or base, for example, with calcium oxide, or the reaction of a water-soluble salt of ortho-phosphoric acid with an appropriate salt or base, for example, trisodium phosphate with calcium chloride. Phosphates having the desired proportions of three or more equivalents of metal or base for each phosphate group may be obtained by the use of stoichiometric proportions in the double decomposition reactions.

Depending upon the particular conditions employed in the preparation of phosphates, a variety of differently constituted products may be obtained. These include the normal ortho phosphates which contain two phosphate groups per molecule such as tricalcium phosphate, its hemi-hydrate $2Ca_3(PO_4)_2.H_2O$, which is believed by some to be the salt, $Ca_3H_2P_2O_9$, of the diatomic acid, $H_8P_2O_9$, which contains the equivalent of two phosphate groups per molecule, and other hydrates, as well as such preferred phosphates as the hydroxy apatites, such as hydroxy apatite (calcium hydroxy hexaphosphate) $3Ca_3(PO_4)_2.Ca(OH)_2$, which contains the equivalent of six phosphate groups per molecule, and like phosphates having an apatite lattice. However constituted, the phosphates used in the process are derivatives of ortho-phosphoric acid even though, in a strict sense, they may not be ortho-phosphates, but may more properly be considered as salts of those phosphoric acids which have at least as much water of constitution as ortho-phosphoric

acid, and in which salts at least three equivalents of base are associated in the compounds for each phosphate group.

Where colorless beads are desired, the use of achromatic or colorless phosphates is preferred. These phosphates are obtained with metals having colorless oxides such as aluminum, magnesium, calcium, barium, strontium, zinc and cadmium.

The amount of phosphate suspension stabilizer used can be varied widely, according with the activity of the stabilizer, the size of beads desired, and the amount of extender used. Generally, the amount will be from 0.05% to 5% or more of the weight of the total suspension, and preferably from 0.1% to 1%. Sufficient phosphate should be present during the polymerization to ensure that there will be undissolved phosphate particles in the suspension system.

The extender used in the process is sulfonated poly(p-methylstyrene). The monomer for making this polymer is described above. The polymerization reaction for preparing the poly(p-methylstyrene) may be carried out by using methods and catalysts well known in the art for polymerizing styrene; for example, the reaction can be carried out in solution, bulk, emulsion, or suspension. In general, the poly(p-methylstyrene) will have a molecular weight from 5,000 to 300,000.

Sulfonation of the polymer can be effected by known methods using sulfonating agents such as chlorosulfonic acid, sulfonyl chloride, or oleum. Generally, the reaction is carried out in a suitable solvent, such as methylene chloride, and at ambient temperatures, although warming can be used to speed up the reaction. Preferably, the poly(p-methylstyrene) is sulfonated to the extent of 0.1% to 15% of sulfonic acid groups per monomer unit.

The polymerization initiators should be soluble in the p-methylstyrene. Thus, non-limiting examples of catalysts are benzoyl peroxide, acetyl peroxide, ditertiary-butyl peroxide, lauryl peroxide, t-butyl perbenzoate, t-butyl peroxypivalate, t-butyl peroctoate, t-butyl peroxyisobutyrate, t-butyl peracetate, and combinations of these.

The amount of catalyst may be varied according to the nature and activity of the particular catalyst, according to the nature of the particular polymerizable material, and according to the product desired.

The suspension polymerization system can contain, usually in the organic (i.e., monomer) phase various dissolved organic substances, including lubricants (for subsequent molding operational), anti-oxidants, dyes, and chain transfer agents. These materials generally have only a moderate or no influence on the particle size of the polymer beads. Lubricants can be of various types, including mineral lubricating oils, fatty esters, such as butyl stearate, and long chain fatty acids, such as stearic and oleic acids. The anti-oxidants, well-known in the art, can include butylated hydroxy toluene, e.g., 2,6-di-t-butyl-p-cresol.

The polymerization is usually carried out at temperatures of about 90°C. The suspension system of this invention, however, is stable at temperatures of as high as 150°C. The advantages of higher polymerization temperature are an accelerated polymerization rate, greater conversion of monomer, and elimination of residual peroxide.

EXAMPLE

A sample (11.8 g.) of poly(paramethylstyrene) (PPMS), which had been prepared by anionic polymerization and which had a nominal molecular weight of 45,000, was dissolved in 106 g. of methylene chloride and reacted with

1.6 g. of chlorosulfonic acid by stirring overnight at room temperature. The resulting mixture was then stirred for several hours with a few drops of water to hydrolyze any chlorosulfonic acid groups.

The resulting product was used as an extender for a paramethylstyrene suspension polymerization. A standard polymerization of paramethylstyrene was carried out by agitating 25 g. of paramethylstyrene containing 0.05 g. of benzoylperoxide and 0.04 g. of t-butylperbenzoate together with 25 g. of water containing 0.25 g. of tricalcium phosphate in a nitrogen atmosphere for 18 hours at 92°C. Varying amounts of different suspension extenders were added to this standard mixture as indicated in the following Table.

Table

| Run No. | Suspension Extender | Amount, ppm | Results |
|---|---|---|---|
| 1 | Potassium Persulfate | 80 | Suspension Collapse |
| 2 | Potassium Persulfate | 160 | Suspension Collapse |
| 3 | Sodium Alkyl Aryl Sulfonate | 69 | Suspension Collapse |
| 4 | Sodium Alkyl Aryl Sulfonate | 46 | Beads |
| 5 | Sodium Alkyl Aryl Sulfonate | 23 | Suspension Collapse |
| 6 | Sulfonated PPMS | 10 | Beads |
| 7 | Sulfonated PPMS | 100 | Beads |

From the data in the Table, it will be noted that potassium persulfate was not effective as an extender. Sodium alkyl aryl sulfonate, a typical anionic surfactant, has a limited range of utility, as was indicated hereinbefore. It was effective at 46 ppm, but not at the higher and lower concentrations, 69 and 23 ppm

respectively. On the other hand, the sulfonated poly(p-methylstyrene) was effective at concentrations as low as 10 ppm and as high as 100 ppm, thus being effective over a wide concentration range. The sulfonated PPMS was not found to be effective in the suspension polymerization of styrene.

WHAT IS CLAIMED IS:

1. A process for the aqueous suspension polymerization of p-methylstyrene, in which a difficultly soluble phosphate is used as a suspension stabilizer and sulfonated poly(p-methylstyrene) as an extender.

2. A process according to claim 1 in which the sulfonated poly(p-methylstyrene) contains 0.1 to 15% of sulfonic acid groups per monomer unit.

3. A process according to claim 1 or 2 in which the amount of sulfonated poly(p-methylstyrene) present in the aqueous suspension is from 10 to 100 ppm.

4. A process according to any of claims 1 to 3 in which the sulfonated poly(p-methylstyrene) is a sulfonated poly(p-methylstyrene) having a molecular weight from 5,000 to 300,000.

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Application number

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# EUROPEAN SEARCH REPORT

EP 80 30 3814

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim |
|---|---|---|
| | US - A - 2 594 913 (J.M. GRIM) * Claims 1,2; column 3, lines 1-15; column 5, lines 1-24 * | 1 |
| | -- | |
| | GB - A - 859 330 (KOPPERS CO.) * Claim 1; page 5, lines 7-24 * | 1 |
| | ---- | |

CLASSIFICATION OF THE APPLICATION (Int. Cl.[3])

C 08 F 12/12
C 08 F 2/18

TECHNICAL FIELDS SEARCHED (Int. Cl.[3])

C 08 F 12/12
212/12
2/18-
2/20
8/36

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| The Hague | 29-12-1980 | CAUWENBERG |

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